

KINETICS OF THE THERMAL DISSOCIATION
OF SILVER NITRITE

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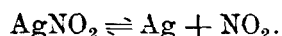
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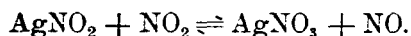
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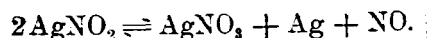
Thorough experiments on the decomposition of silver nitrite were performed as early as 1871 by E. Divers 1). According to Centnerszwer and Chęciński 2) this reaction under atmospheric pressure takes the following course:



The escaping NO_2 reacts with the unchanged nitrite:



The following equation is obtained from this for the total reaction:



To the pressure of one atmosphere there corresponds a dissociation temperature of 132° centigrade, and to a pressure of one millimeter mercury: 91°. The system is a four-phase one (AgNO_2 , AgNO_3 , Ag and the gaseous phase) According to the Gibbs - Ostwald rule there are three components present. The system is therefore univariant.

The kinetic experiments were performed with the apparatus as described previously 3). The glass tube with the dissociating substance was filled with nitrogen and heated in the electric oven. During the experiment the increase of either the volume or of the pressure of the gas was measured. Two test series were performed: an isobaric and an isochoric one. In the isobaric series the generated gas under constant pressure was collected in the gas-measuring tube and the volumes were measured with an accuracy of 0.1 ccm=0.1 mg. In the isochoric series the reaction chamber was closed by a differential pressure gauge. The increase in pressure was measured during the decomposition on

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*) Numbers in the margin indicate pagination in the original foreign text.

1) E. Divers, Journ. of the Chemical Society, London (2) 9, 85 (1871)

2) M. Centnerszwer and T. Chęciński, this bulletin 1935, pg. 156

3) M. Blumenthal, Journ. Chimie Physique, 31, 490 (1934).

the differential pressure gauge. For the fluid for the pressure gauge we used bromonitronaphthalene. The accuracy of the observations was $1\text{mm}=0.01\text{ mg}$. In some cases mercury was used as the fluid for the pressure gauge.

The silver nitrite produced by us crystallized in long fibers of a yellowish colour. The diameter of the individual crystals was about 0.02 mm ; their length varied appreciably, but was on the average about 1 cm . The crystals were dried carefully in vacuo at 40° before being used for the experiments. The question arose whether the association of the NO_2 to N_2O_4 and the dissociation of the NO_2 into NO and O could possibly have a disturbing influence. But since the temperature during the experiments lay only between 100° and 300° , the influence of these secondary reactions could be neglected.

If the reaction takes place in a vacuum, the NO_2 has no time to oxidize the silver nitrite and escapes very fast from the surface. Ag and NO_2 appear then as the only decomposition products. But with increasing pressure NO is produced in the gas-phase in ever increasing quantities. We have chosen from the above mentioned paper by Centnerszwer and Chęciński five experiments which were performed at 195° under different pressures. They are compiled in Table I.

Table I.

Pressure	1	25	50	200	760 mm Hg
% NO_2	99.7	61.4	29.4	24.2	0
% NO	0.3	38.6	70.6	75.8	100

The reactions which take place can be considered as chain reactions:

The generated silver crystals separate from the silver nitrite in a later phase of the reaction and the growing silver nitrite too shows a tendency to form larger crystals. However, during the first half of the reaction the crystalline structure of the silver nitrite remains unchanged and the reaction products separate uniformly on its surface. / 168

The NO content of the gaseous phase declines continually at rising temperature as can be seen from the following Table II:

Table II

Temperature	195°	230°	300°
% NO_2	0	18.2	28.1
% NO	100	81.8	71.9

The results of the kinetic experiments at 175° and at a pressure of one atmosphere are shown in Table III. The volume of the collected gas is listed under v , the state of decomposition in % under x and the calculated reaction velocity dx/dt is listed under I as the mean from two test series.

Table III

Weight of sample: 0.3g. $t=175^{\circ}$

Time t in min.	10	22	27	43	64	108
v in ccm	2.05	4.15	6.20	8.30	10.35	12.4
x in %	10	20	30	40	50	60
I	0.205	0.244	0.244	0.131	0.098	0.060

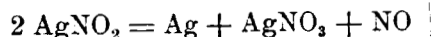
At 175° there appears a distinct induction period during the first 27 minutes.

Table IV

Weight of sample: 0.25g. $t=195^{\circ}$

t in Min.	2.5	5.0	8	12	19	34	64	123
v in ccm	1.9	3.8	5.7	7.7	9.6	11.4	13.4	15.3
x in %	10	20	30	40	50	60	70	80
I	0.760	0.760	0.633	0.500	0.271	0.120	0.066	0.031
$100 K_2$	—	0.500	0.503	0.505	0.526	0.441	0.361	0.325

The induction period is shorter at 195° : it is only five minutes. / 169
According to the reaction equation:



we have to expect a bimolecular reaction:

$$\frac{dx}{dt} = K_2(1-x)^2.$$

The calculated constants K_2 are given in Table IV and show satisfactory agreement. Only toward the end of the experimental series the reaction constants become smaller. It seems therefore that the reaction products hamper the decomposition. In Tables V and VI we show the results obtained at 215° and 300° .

Table V

Weight of sample: 0.15g. $t=215^\circ$

t in Min.	1	2	4	7	10.5	13.6	21	49	83
v in ccm	1.15	2.30	3.45	4.60	5.75	6.70	7.85	9.20	10.35
x in %	10	20	30	40	50	60	70	80	80
I	1.15	1.15	0.57	0.38	0.33	0.29	0.15	0.05	0.03
$10 K_1$	—	0.124	0.107	0.095	0.100	0.110	0.111	0.110	0.083

Table VI

Weight of sample: 0.3g. $t=300^\circ$

t in Min.	1	2	3	4	6.5	8.5	12	18
v in ccm	4.2	6.2	8.3	10.3	12.4	14.7	16.8	18.8
x in %	20	30	40	50	60	70	80	90
I	4.20	2.10	2.10	2.10	0.90	1.05	0.60	0.33
$K_{1.5}$	0.119	0.100	0.097	0.103	0.097	0.103	0.104	0.120

At higher temperatures (215° and 300°) there is generated in the gas phase NO_2 in ever increasing quantities. The constant calculated from the equation of second order shows at 215° still a very good agreement. But at 300° the order of the reaction becomes smaller. We used the following empirical formula: / 170

$$\frac{dx}{dt} = K_{1.5}(1-x)^{1.5}.$$

This corresponds to the kinetics of a reaction with side reactions, which also agrees with the actual course of the dissociation.

Experiments at constant volume.

In experiments that were performed in a vacuum (or at very low initial pressures) there appeared in the gas phase only NO_2 , whereas the gas phase in other experiments consisted of NO and NO_2 in different proportions. We show in the Tables VII, VIII and IX the results of three test series which were performed at 150° under different initial pressures. The pressure increases, denoted by p , are listed according to the readings of the pressure gauge which was filled with nitrobrmonaphthalene, I is the reaction velocity; x denotes, as before, the respective degree of decomposition.

Table VII

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Weight of sample: 0.4g. $t=150^\circ$. Initial pressure=1mm Hg. Pressures in the nitro-bromonaphthalene scale.

t in Min.	6	12	18	24	30
p in mm	181	282	350	417	475
x in %	16	25	29	37	42.0
$I = \frac{dt}{dp}$	30.1	16.8	11.3	11.1	9.7

Table VIII

Weight of sample: 0.4g. $t=150^\circ$. Initial pressure 200 mm Hg. Pressures in the nitro-bromonaphthalene scale.

t in Min.	5	11	20	29	38	59
p in mm	68	118	178	239	298	420
x in %	6	11	16	21	26	37
$I = \frac{dt}{dp}$	13.6	4.55	6.66	6.77	6.55	5.81

Table IX

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Weight of sample: 0.4g. $t=150^\circ$. Initial pressure 760 mm Hg. Pressures in the nitro-bromonaphthalene scale.

t in Min.	3	6	9	12	15	21	24	30	78
p in mm	12	25	40	50	66	83	93	102	232
x in %	1	2	3	4	5	7	8	9	20
$I = \frac{dp}{dt}$	4.00	4.33	5.00	3.33	5.33	5.66	3.33	1.50	2.29

If we calculate the reaction velocities for the degree of decomposition of 20% of the initial amount, then we obtain for the three pressures (1 mm, 200 mm and 760 mm) as the ratio of the reaction velocities:

$$I_1 : I_2 : I_3 = 11 : 6 : 3.$$

We see from this that the reaction velocity decreases when the initial pressure increases. Which is quite understandable since the distance of the system from the state of equilibrium decreases with rising pressure.

It is to be noted that when the system stays under the initial pressure of 1 mm Hg, the corresponding temperature of equilibrium is comparatively low.

Therefore, the initial velocity is rather high. But it decreases rapidly with rising pressure and when the system approaches equilibrium thereby. But in those experiments which were performed under the initial pressures of 200 mm and 760 mm the distance of the system from the state of equilibrium was smaller:: hence the decline of the initial velocity is smaller and a distinct induction period appears in these cases. At 150° it is not yet very apparent. But it becomes much more distinct at temperatures of 175° and 195° as can be seen from the following results.

Table X

Weight of sample: 0.4g. $t=175^\circ$. Initial pressure = 1mm Hg. Pressures in Hg scale.

t in Min.	1	2	3	5	9	15	23	30	135
p in mm	10	24	35	53	77	102	122	147	246
x in %	—	10	—	—	30	40	50	60	90
$I = \frac{dp}{dt}$	10	14	11	8.0	5.3	4.1	2.5	3.5	0.95
K_1	—	—	—	—	0.040	0.034	0.030	0.030	—

Table XI

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Weight of sample: 0.3g. $t=195^\circ$. Initial pressure 1 mm Hg. Pressures in Hg scale.

t in Min.	2	2	3	4	6	8	12	18	27
p in mm	20	40	66	84	109	128	154	174	196
x in %	10	20	30	40	50	60	70	80	90
$I = \frac{dp}{dt}$	20	20	26	18	12.5	9.5	6.5	3.3	2.4
K_1	—	—	—	0.127	0.115	0.114	0.100	0.090	0.080

The reaction at higher temperatures, after the termination of the induction period, takes place according to an equation of first order. The constants K_1 calculated from this equation show a good agreement. Only in the last stages of the reaction a hampering influence of the reaction products makes itself felt.

If we apply the Arrhenius equation

$$\log K = -\frac{A}{T} + B,$$

to the velocity constants, then we can calculate from the thus gained numbers the "activation energies" A . The results are compiled in Table XII.

Table XII

Temperature	$P = 760 \text{ mm}$	$P = 1 \text{ mm}$
150°—175°	$A = 41080 \text{ cal.}$	$A = 13370 \text{ cal.}$
175°—195°	26820	12030
195°—215°	12405	—

We see from Table XII that the activation energy rises with higher pressure and decreases with higher temperature.

Summary

1) The kinetics of the thermal decomposition of silver nitrite was investigated.

2) The reaction takes place in two stages: (I) $\text{AgNO}_2 = \text{Ag} + \text{NO}_2$ and (II) $\text{NO}_2 + \text{AgNO}_2 = \text{AgNO}_3 + \text{NO}$. The velocities of both reactions depend on the pressure.

3) When performed in a vacuum, the reaction takes place according to an equation of first order, but when performed under atmospheric pressure, according to the equation of second order. The order of the reaction becomes lower with rising temperature. / 173

4) An induction period appears in the vicinity of the equilibrium state. It becomes more pronounced the higher the temperature is, but vanishes at a certain distance from the temperature of equilibrium.

We wish to express here our gratitude to Prof. M. Centnerszwer for his stimulating suggestions and his continuing interest.

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